

Stability of perovskite-type clusters in melts for relaxor ferroelectric crystal growth

Zengzhe Xi · Wei Long · Jiangnan Liu · Peng Liu ·
Zhenrong Li · Xi Yao

Received: 16 March 2007 / Accepted: 26 September 2007 / Published online: 13 October 2007
© Springer Science + Business Media, LLC 2007

Abstract Relaxor ferroelectric single crystals with perovskite structure were novel materials which might revolutionize some applications in medical ultrasonic imaging, telecommunication and ultrasonic devices. But during crystal growth and melt solidification, pyrochlore-type phase presented now and then, which reduced the integrality and properties of ferroelectric single crystals. This work dealt with the stability of perovskite-type clusters in melts for relaxor ferroelectric crystal growth by quenching and slow cooling. Differential thermal analysis (DTA) and X-ray diffraction (XRD) were employed to ascertain the transformation temperature between perovskite-type and pyrochlore-type clusters. Investigated results indicated that clusters in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}32\text{PbTiO}_3$ (PMN–32PT) melt which was under suitable temperature and prepared by proper pre-synthetic method were all and singular of perovskite-type structure, which established the fundament of PMN–32PT relaxor ferroelectric crystal growth from melts by Bridgman method. Whereas, clusters in $\text{Pb}(\text{Zn}_{1/3}$

$\text{Nb}_{2/3})\text{O}_3\text{-}9\text{PbTiO}_3$ (PZN–9PT) melt were of perovskite-type structure, pyrochlore-type structure, homologous PbO structure or homologous ZnO structure. During crystal growth from melts by Bridgman method, the pyrochlore phase always appeared.

Keywords Perovskite · Pyrochlore · Ferroelectric · Crystal

1 Introduction

Since $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN–PT) [1] and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN–PT) [2, 3] single crystals were grown to a size satisfying the demand of property test, relaxor ferroelectric single crystals became researching hotspot in piezoelectric material territory. In the last decade, there were thousands literatures reporting investigated results about the growth, structure and properties of many kinds of relaxor-based ferroelectric single crystals. It was indicated that these crystals were of perovskite structure and much higher piezoelectric, pyroelectric, electrostriction and electromechanical coupling properties than conventional $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) ceramics [4–6]. These crystals would get revolutionary applications in ultrasonic, marine acoustic, large strain actuator, condensed energy storage, smart and micro electronic mechanical system (MEMS) systems. In many literatures [7, 8] Bridgman and flux-based method were employed to grow these crystals. For example PMN–PT crystals were grown by Bridgman-based technique from approximately stoichiometric melts, and PZN–PT crystals were grown from high temperature solutions composed by stoichiometric raw materials and PbO as solvent. During perovskite crystals growth, pyrochlore-type phase crystallized sometimes, which reduced the integrality and properties of perovskite-type single crystals. Improving the

Z. Xi (✉) · W. Long · J. Liu
School of Materials and Chemical Engineering,
Xi'an Technological University,
Jinhua Road,
Xi'an 710032, China
e-mail: zzx@mail.xjtu.edu.cn

P. Liu
School of Physics and Information Technology,
Shaanxi Normal University,
Chang'an Road,
Xi'an 710062, China

Z. Li · X. Yao
Electronic Materials Research Laboratory,
Key Laboratory of Education Ministry, Xi'an Jiaotong University,
Xianning Road,
Xi'an 710049, China

growth technique, pyrochlore-type phase could be reduced or restrained. Virtually, in melts there were homologous crystalline clusters caused by structure up-and-down. The structure, size, amount and distribution of clusters varied with melt temperature. Below melting or solidus temperature, these clusters could become the nucleation of crystallization. So the status of clusters in melts should influence the processes and results of solidification. This paper dealt with the status of umpty melts, intentionally searched after the cause of pyrochlore-type phase in the growth of relaxor ferroelectric crystals.

2 Experimental procedure

High purity (better than 99.95%) PbO, MgO, ZnO, Nb₂O₅ and TiO₂ powders were used as starting materials. Firstly, MgO and Nb₂O₅ were mixed and calcinated at 1000°C for 6 hours to form MgNb₂O₆. ZnO and Nb₂O₅ were mixed and calcinated at 1000°C for 6 hours to form ZnNb₂O₆. Then mixtures of PbO, MgNb₂O₆, TiO₂ powders in (100-*x*) (PMN-32PT)-*x*PbO (*x*=0, 10 at %, the same below) as well as PbO, ZnNb₂O₆, TiO₂ powders in 90(PZN-9PT)-10PbO were prepared respectively by ball milling for 6 h. The mixture in 95(PMN-32PT)-5PbO was made from PbO, MgO, Nb₂O₅ and TiO₂ powders by ball milling for 6 hours. Each mixture about 20 g was filled into a Pt crucible and then the Pt crucible was sealed by a special way to avoid the evaporation of PbO. The Pt crucible was put into an alumina crucible which had the same shape as Pt crucible. The Pt crucible held by alumina crucible was put into the vertical furnace and heated to high temperature for 1.5 h. Then the

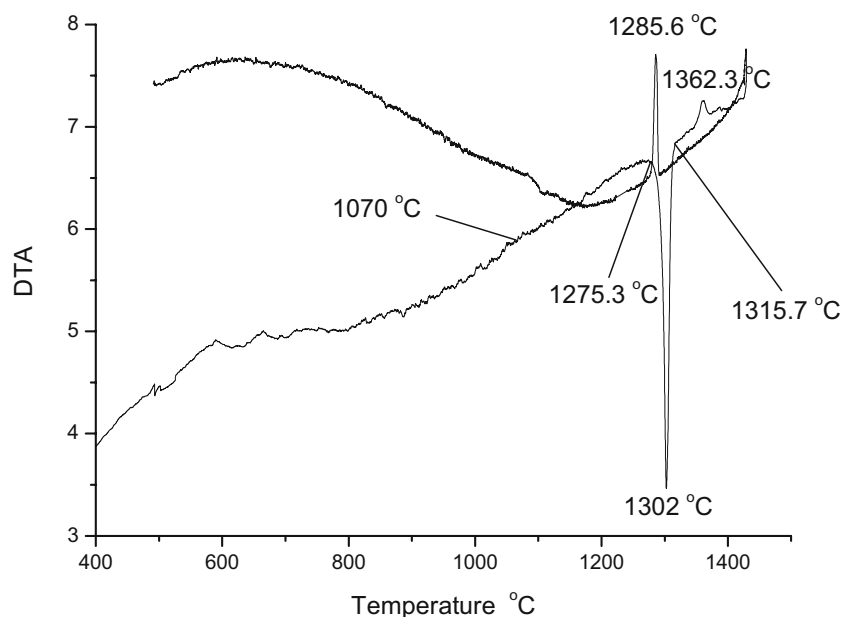
mixture together with crucible was quenched into water or cooled in situ with furnace or subjected to heat-cooling circulations in situ. The ground powders quenched or cooled in situ were analyzed by Rigaku D/max-2400 X-ray diffraction (XRD) meter with a source of Cu K_α. Each mixture about 40 mg was filled into a Pt crucible (2.0 mm in diameter and 3.5 mm in depth) and then the Pt crucible was sealed in the same way as for quenching experiment to avoid the evaporation of PbO. The ready crucibles were used for differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Thermal analyses were performed on TA2000 and NETZSCH STA 499C analyzer at a heating rate of 10°C/min. PZN-9PT relaxor crystals were grown by a normal flux method from 45(PZN-9PT)-55PbO solution which was heated to 1100°C. Mixture in 90(PZN-9PT)-10PbO was subjected to the same process as crystal growth of PMN-32PT by Bridgman method [9, 10] in which the melt was held at 1400°C.

3 Results and discussion

3.1 Experiment based on PMN-32PT

Figure 1 showed the DTA result of PMN-32PT mixture powders. There was no obvious exothermic/endothermic peak on the heating curve from room temperature to about 1280°C. But a gradually endothermic process, corresponding to the solid reaction of PbO, MgNb₂O₆ and TiO₂, could be observed from about 600°C to 1070°C. Then a sharp endothermic peak, corresponding to the melting process of the mixture, appeared at 1302°C and ranged from 1275.3 to 1362.3°C.

Fig. 1 A DTA curve of PMN-32PT mixture



1315.7°C. Whereafter, an exothermic peak presented at 1362.3°C. Analogous exothermic peaks on DTA curves of $(1-x)\text{PMN}-x\text{PT}$ ($x=0.10, 0.20, 0.30, 0.35, 0.40, 0.45, 0.55, 0.65, 0.75, 0.85$) were reported in our previous paper [11]. These exothermic peaks indicated some unknown transformation in melts. There was a sharp exothermic peak at 1285.6°C on the cooling curve, which corresponded to melt solidification.

For searching after the transformation corresponding to the exothermic peak at 1362.3°C, PMN–32PT melts were held at temperatures of 1300, 1320, 1340, 1380, 1420 and 1460°C respectively for 1.5 h and then quenched. Quenched specimens manifest a status as grey homogeneous solid with some pores. This status was different from PMN–32PT crystals as reported. Figure 2 showed XRD results of Quenched specimens ground with a carnelian mortar. Labeled peaks corresponded to perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ based phase. Non-labeled peaks corresponded to pyrochlore $\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$ based phase (similarly hereinafter). Curves corresponding to melting temperature below 1380°C showed pure perovskite phase in quenched specimens. There were peaks corresponding to pyrochlore based phase on curves corresponding to melting temperature at 1420 and 1460°C. It was indicated that in PMN–32PT melt, clusters were all and singular of perovskite-type structure below about 1380°C, but partially of pyrochlore-type structure over about 1420°C. In search of the critical temperature, the melt held at 1380°C was cooled in situ with furnace. The solidified sample showed yellow inhomogeneous solid. This sample was also analyzed by XRD. Pyrochlore-type structure trail appeared on the curve labeled as 1380°C-normal in Fig. 2. The XRD spectrum

of the sample which was subjected to heat-cooling circulations (being heated to 1380°C, held for 1.5 h and cooled to room temperature, circulating the process for six times) was labeled as 1380°C-manytimes in Fig. 2. It was observed that the sample was almost all of pyrochlore-type structure. It was deduced that, the critical temperature was below and near 1380°C. At the temperature, the structure of clusters transformed from perovskite-type to pyrochlore-type. In addition, kinetic rates of nucleations by these two kinds of clusters were different. There were a great number of perovskite-type clusters and a little number of pyrochlore-type clusters in PMN–32PT melt at 1380°C. While the melt was being quenched, crystals nucleated by perovskite-type clusters instead of by pyrochlore-type clusters. Under normal solidification condition, pyrochlore-type clusters took part in nucleation. Being subjected to heat-cooling circulations, crystals nucleated major by pyrochlore-type clusters during subsequent solidification.

In practical preparation of relaxor PMN–32PT single crystals, the raw material usually consisted of stoichiometry and excessive PbO instead of strict stoichiometry. 90(PMN–32PT)–10PbO mixture was chosen for quenching experiments too. Mixtures in 90(PMN–32PT)–10PbO were heated to melt, held at 1350, 1380, 1430 and 1460°C respectively for 1.5 h and then quenched. Quenched samples showed grey homogeneous solid with some pores. XRD spectrums of quenched samples corresponding to the above four holding temperatures shown in Fig. 3 were almost the same as each other. Quenched samples consisted of perovskite-type phase and PbO (labeled by a). No peak of pyrochlore-type phase was detected. It was indicated that clusters in 90 (PMN–32PT)–10PbO melts at temperature ranging from

Fig. 2 XRD spectrum of PMN–32PT powders

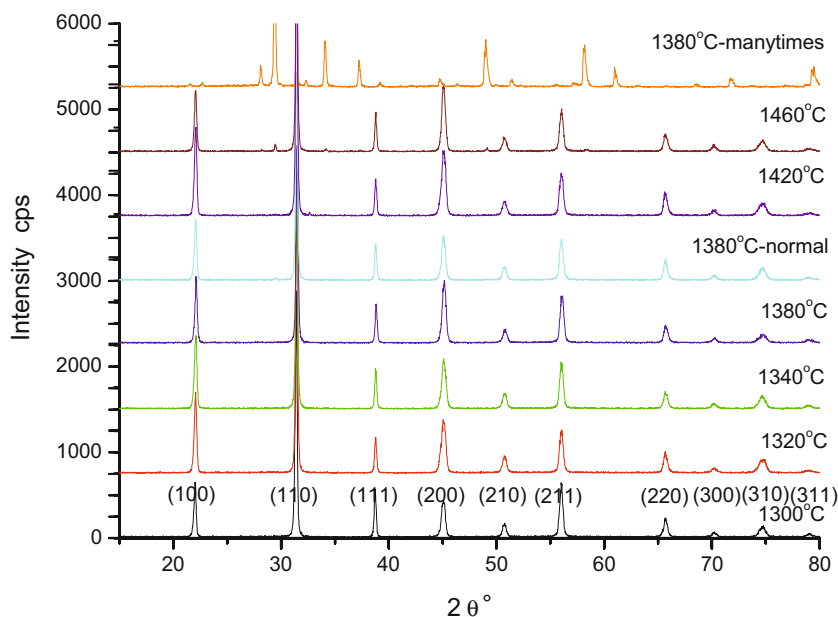
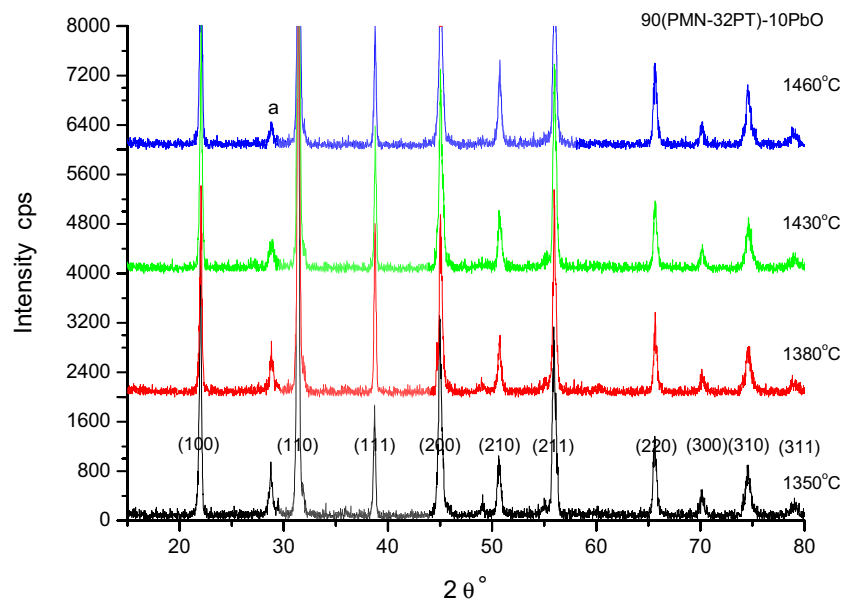


Fig. 3 XRD spectrum of quenched 90(PMN–32PT)–10PbO powders *a*—peak of PbO phase



1350 to 1460°C were all of perovskite-type structure. In comparison with XRD results of PMN–32PT, addition of PbO could raise the stability of perovskite-type clusters as well as the critical temperature at which perovskite-type clusters transformed to pyrochlore-type clusters.

Mixtures in 95(PMN–32PT)–5PbO made directly from PbO, MgO, Nb₂O₅ and TiO₂ powders were quenched by the same method as PMN–32PT and 90(PMN–32PT)–10PbO. Holding temperature was 1280, 1320, 1360, 1400 and 1420°C respectively. Quenched samples showed grey homogeneous solid with some pores. XRD spectrums of quenched samples corresponding to five holding temper-

atures shown in Fig. 4 were almost the same as each other. Quenched samples consisted of perovskite-type phase, pyrochlore-type phase, PbO (labeled by *a*) and Pb₃O₄ (labeled by *b*). In comparison with XRD results of PMN–32PT and 90(PMN–32PT)–10PbO, much pyrochlore-type phase appeared. It was indicated that preparing technology strongly affects the melt status. In relaxor PMN–32PT single crystal growth, pre-synthetic MgNb₂O₆ was necessary. Seeing straightly the difference of situs between diffraction peaks of phases in PMN–32PT, 90(PMN–32PT)–10PbO and 95(PMN–32PT)–5PbO, several typical XRD spectrums were shown in the same one coordinate

Fig. 4 XRD spectrum of quenched 95(PMN–32PT)–5PbO powders *a*—peak of PbO phase, *b*—peak of Pb₃O₄ phase

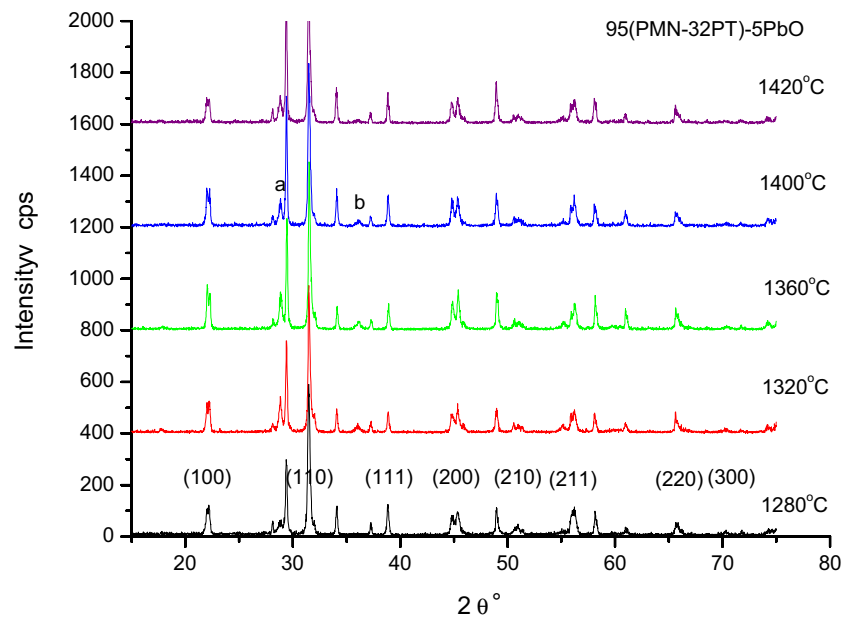
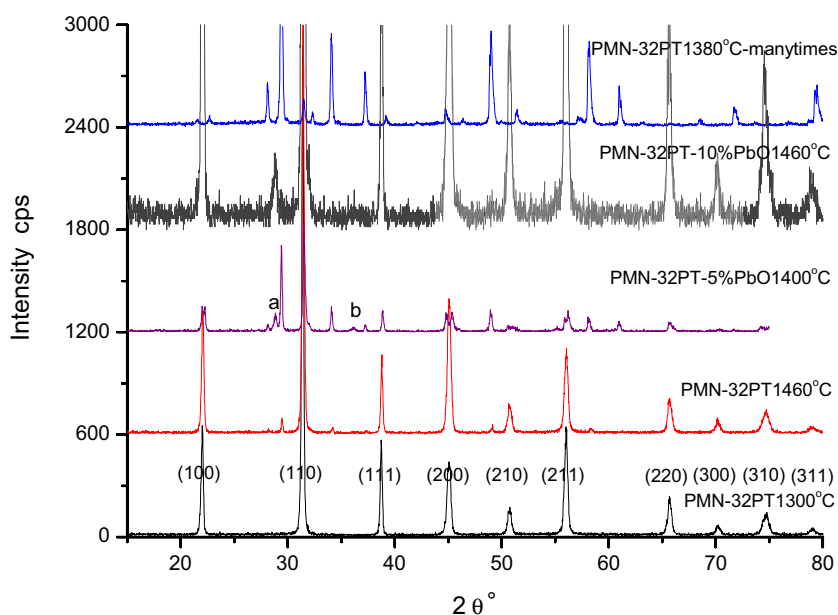


Fig. 5 several typical XRD spectrums *a*—peak of PbO phase, *b*—peak of Pb_3O_4 phase



system in which *a* corresponded to PbO phase, while *b* corresponded to Pb_3O_4 phase (as shown in Fig. 5).

3.2 Experiment based on PZN–9PT

Figure 6 showed the DSC result of PZN–9PT mixture powders. There was no obvious exothermic/endothermic peak on the heating curve from room temperature to about 1202°C. But a gradually endothermic process, corresponding to the solid reaction of PbO, MgZn_2O_6 and TiO_2 , could be observed from about 913 to 1202°C. There were two endothermic peaks, corresponding to the melting process of

the mixture and transformation of clusters in the melt, appearing at 1231.0 and 1278.2°C respectively.

For searching after the status of melt, mixtures in 90 (PZN–9PT)–10PbO were quenched by the same technology as that in 90(PMN–32PT)–10PbO. Holding temperature was 1240, 1280, 1320, 1360 and 1400°C respectively. Quenched samples showed grey non-homogeneous solid with some yellow granules. XRD spectrums of quenched samples corresponding to five holding temperatures were shown in Fig. 7. XRD results of powders ground with PZN–9PT relaxor crystals grown by flux method from 45(PMN–32PT)–55PbO solution and crystals grown by Bridgman

Fig. 6 A DSC curve of PZN–9PT mixture

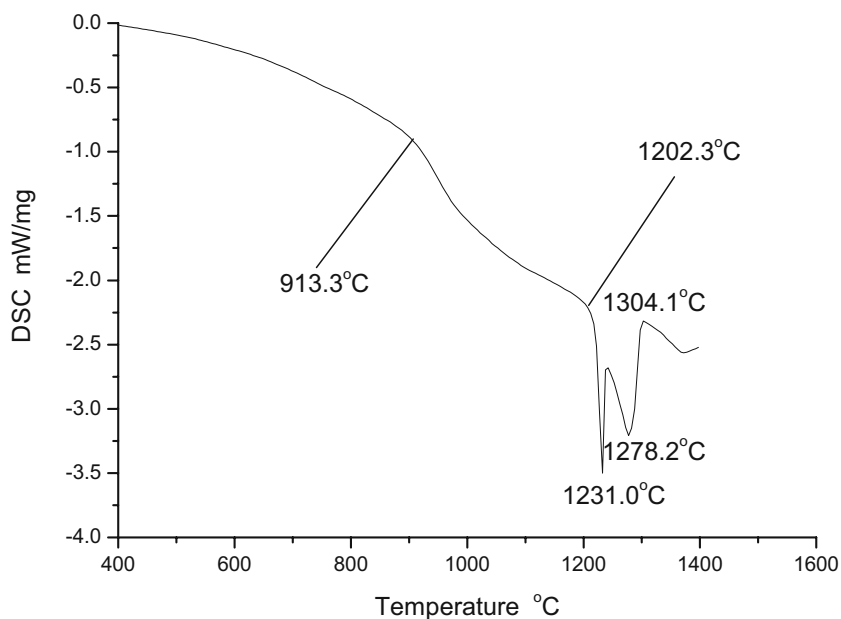
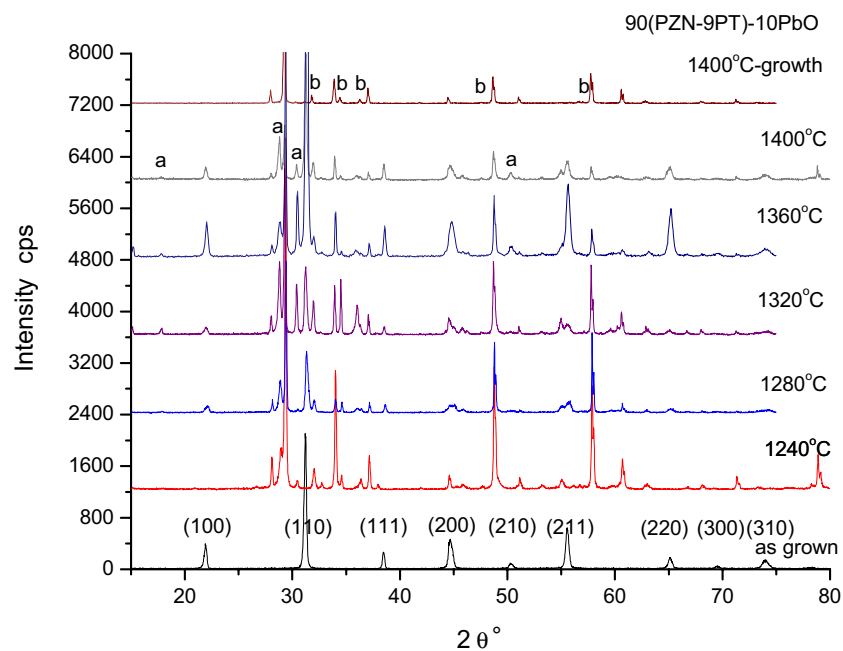


Fig. 7 XRD spectrum of PZN–9PT-based powders *a*—peaks of PbO phase, *b*—peaks of ZnO phase

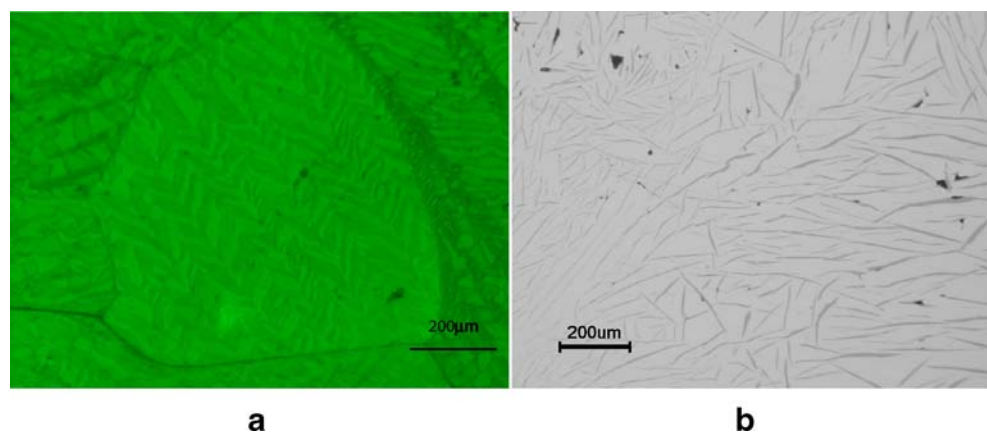


method from 90(PMN–32PT)–10PbO melt at 1400°C were labeled by as grown and 1400°C-growth respectively in Fig. 7. Labeled peaks corresponded to perovskite $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ based phase. Non-labeled peaks corresponded to pyrochlore $\text{Pb}_{1.83}\text{Zn}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$ based phase (similarly hereinafter). Peaks corresponding to PbO were labeled by *a*. Peaks corresponding to ZnO were labeled by *b*. The as grown crystal of PZN–9PT was of pure perovskite phase structure. No perovskite phase was detected in the quenched sample corresponding to the holding temperature at 1240°C, which meant clusters in the melts at lower temperature were of pyrochlore-type structure, homologous PbO structure or homologous ZnO structure. Quenched samples corresponding to the holding temperature ranging from 1280°C to 1400°C were composed of perovskite phase, pyrochlore-type phase, PbO and ZnO, which meant clusters in

the melts at higher temperature were of pyrochlore-type structure, perovskite-type structure, homologous PbO structure or homologous ZnO structure. Crystals grown by Bridgman method from 90(PMN–32PT)–10PbO melt at 1400°C were composed of pyrochlore $\text{Pb}_{1.83}\text{Zn}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$ based phase and ZnO, which meant pyrochlore-type clusters were more kinetic-prior in nucleation than perovskite-type clusters.

Being subjected to the same growth process by Bridgman method in which the temperature of melt was 1400°C, pulling rate was 0.3 mm/h, 90(PMN–32PT)–10PbO and 90(PZN–32PT)–10PbO got different microstructure, as shown in Fig. 8. The former was composed of perovskite-type crystal grains in which there were ferroelectric domains. The latter was composed of pyrochlore-type crystal grains in which there were some band-shape tesseras, perhaps being ZnO or PbO, without domains.

Fig. 8 Microstructure of as grown PMN–32PT and PZN–9PT crystals (a) PMN–32PT, (b) PZN–9PT



4 Conclusion

- (1) The exothermic peak on the DTA curve of PMN–32PT corresponded to the transformation of clusters from perovskite-type structure to pyrochlore-type structure.
- (2) The addition of PbO could raise the stability of perovskite-type clusters as well as the critical temperature at which perovskite-type clusters transformed to pyrochlore-type clusters in PMN–32PT melt.
- (3) Status of PMN–32PT based melts were strongly affected by pre-synthetic process.
- (4) Clusters in PMN–32PT melt, being under suitable temperature and prepared by proper pre-synthetic method, were all and singular of perovskite-type structure, which established the fundament of PMN–32PT relaxor ferroelectric crystal growth from melts by Bridgman method. Whereas, clusters in PZN–9PT melt were of perovskite-type structure, pyrochlore-type structure, homologous PbO structure or homologous ZnO structure. During crystal growth from melts by Bridgman method, the pyrochlore phase always appeared.

Acknowledgements This work was supported by the National Natural Science Foundation of China No. 50572059, the item of Shaanxi Education Hall No. 06JK277, Xi'an Science Technology Bureau No. GG05060, and the Natural Science Foundation of Xi'an Jiaotong University.

References

1. J. Kuwata, K. Uchino, S. Nomura, *Jpn. J. Appl. Phys.* **21**(9), 1298 (1982)
2. T.R. Shrout, Z.P. Chang, N. Kim, S. Markgraf, *Ferroelectr. Lett.* **12**, 63 (1990)
3. Z.-G. Ye, P. Tisso, H. Schmid, *Mater. Res. Bull.* **25**, 739 (1990)
4. F. Robert, *Science*. **275**, 1878 (1997)
5. F. Huaxiang, E. Ronald, *Nature*. **403**, 281 (2000)
6. Y. Tang, X. Zhao, X. Feng, W. Jin, H. Luo, *Appl. Phys. Lett.* **86**(8), 082901 (2005)
7. C.B. DiAntonio, F.A. Williams Jr., S.M. Pilgrim, W. A. Schulze, C. Feng, Z. Yin, *IEEE International Symposium on Application of Ferroelectrics*, 431 (2002)
8. L. Zhang, M. Dong, Z.-G. Ye, *Mater. Sci. Eng. B78*, 96 (2000)
9. Z. Xi, X. Yao, Z. Li, Z. Xu, *Ceram. Int.* **30**, 1691 (2004)
10. Z. Xi, Z. Li, Z. Xu, X. Yao, *Ferroelectrics*, **332**, 105 (2006)
11. Z. Li, Z. Xi, Z. Xu, X. Yao, *Ferroelectrics*, **326**, 31 (2005)